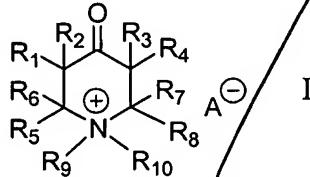


What is claimed is:

1. A method of producing mostly $5\beta,6\beta$ -epoxides of steroids from Δ^5 -unsaturated steroids by an epoxidation reaction using a ketone and an oxidizing agent under conditions effective to generate epoxides.

wherein said ketone is selected from compounds of generic formula I.



R_1 or R_4 in formula (I) is selected from alkyl, halogenated alkyl, aryl, OR (where $R = H$, alkyl or aryl), OCOR (where $R = H$, alkyl or aryl), OCOOR (where $R =$ alkyl or aryl), OCOOCH₂R (where $R =$ aryl), OCONR₁R₂ (where R_1 or $R_2 = H$, alkyl or aryl), OSiR₁R₂R₃ (where R_1 , R_2 or $R_3 =$ alkyl or aryl), and halogen;

R_2 or R_3 in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, OR (where $R = H$, alkyl or aryl), OCOR (where $R = H$, alkyl or aryl), OCOOR (where $R =$ alkyl or aryl), OCOOCH₂R (where $R =$ aryl), OCONR₁R₂ (where R_1 or $R_2 = H$, alkyl or aryl), OSiR₁R₂R₃ (where R_1 , R_2 or $R_3 =$ alkyl or aryl), and halogen;

R_5 , R_6 , R_7 or R_8 in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where $R = H$, alkyl or aryl), and CONR₁R₂ (where R_1 or $R_2 = H$, alkyl or aryl);

R_9 or R_{10} in formula (I) is selected from alkyl, halogenated alkyl, and aryl; and

A in formula (I) is selected from halogen, OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆.

2. The method of claim 1 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

3. The method of claim 2 wherein said epoxidation reaction is carried out using potassium peroxomonosulfate as an oxidizing agent.

4. The method of claim 1 wherein said epoxidation reaction is carried out in a homogeneous solvent system containing dimethoxymethane-acetonitrile-water, acetonitrile-water, acetone-water, dioxane-water, dimethoxyethane-water, tetrahydrofuran-water, or a biphasic solvent system containing dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethylether-water, or mixtures thereof.

5. The method of claim 1 wherein said epoxidation reaction is carried out at a temperature within the range from about -10 °C to about 40 °C.

6. The method of claim 5 wherein said epoxidation reaction is carried out at room temperature.

7. The method of claim 1 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.

8. The method of claim 7 wherein said pH is within the range from about 7.0 to about 7.5.

9. The method of claim 7 wherein said pH is controlled by using a pH-stat or a buffer.

10. The method of claim 9 wherein said buffer is selected from the solutions consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, potassium carbonate, potassium hydroxide, or mixtures thereof.

11. The method of claim 1 wherein said epoxidation reaction provides said epoxides in at least about 5:1 β/α -epoxide ratio.

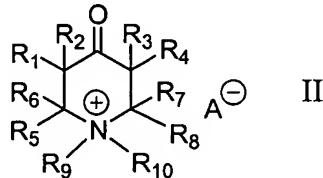
12. A method of producing mostly $5\beta,6\beta$ -epoxides of steroids from Δ^5 -unsaturated steroids having a substituent at the 3α -position by an epoxidation reaction using a ketone and an oxidizing agent under conditions effective to generate epoxides.

13. The method of claim 12 wherein said substituent is selected from OR (where R = H, alkyl or aryl), $O(CH_2)_nOR$ (where n = 1, 2 or 3, R = H, alkyl or aryl), $O(CH_2)_mSO_nR$ (where $n = 1, 2$ or 3; n = 0, 1 or 2; R = H, alkyl or aryl), $OSiR_1R_2R_3$ (where R_1, R_2 or R_3 = alkyl or aryl), OSO_nR (where n = 0, 1 or 2; R = H, alkyl or aryl), OCO_nR (where n = 1 or 2; R = H, alkyl or aryl), $OCONR_1R_2$ (where R_1 or R_2 = H, alkyl or aryl), OPO_nR (where n = 2 or 3; R = alkyl or aryl), NR_1R_2 (where R_1 or R_2 = H, alkyl or aryl), $NR_1CO_nR_2$ (where n = 1 or 2; R_1 or R_2 = H, alkyl or aryl), $NR_1CONR_2R_3$ (where R_1, R_2 or R_3 = H, alkyl or aryl), $NR_1SO_nR_2$ (where n = 1 or 2; R_1 = H, alkyl or aryl, R_2 = alkyl or aryl), $NPhth$ (Phth = phthaloyl group), $^+NR_1R_2R_3$ (where

R_1 , R_2 , or R_3 = H, alkyl or aryl), $SiR_1R_2R_3$ (where R_1 , R_2 , or R_3 = H, alkyl or aryl), SO_nR (where n = 0, 1 or 2; R = H, alkyl or aryl), SCO_nR (where n = 1 or 2; R = H, alkyl or aryl), halogen, CN, NO_2 , alkyl, aryl, COOR (where R = H, alkyl or aryl), and $CONR_1R_2$ (where R_1 or R_2 = H, alkyl or aryl).

14. The method of claim 12 wherein said Δ^5 -unsaturated steroid having a substituent at the 3α -position is selected from the group consisting of Δ^5 -unsaturated steroids having a ketal derivative of ketone group or a thioketal derivative of ketone group at the 3-position.

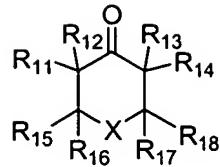
15. The method of claim 12 wherein said ketone is selected from the group consisting of compounds of generic formula II, III, IV, and V wherein



R_1 , R_2 , R_3 , or R_4 in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl), OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl), and halogen;

R_5, R_6, R_7, R_8, R_9 or R_{10} in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and $CONR_1R_2$ (where R_1 or R_2 = H, alkyl or aryl);

A in formula (II) is selected from halogen, OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆;

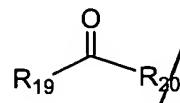


III

X in formula (III) is selected from $(CR_1R_2)_n$ (where $n = 1, 2, 3, 4$, or 5 ; R_1 or $R_2 = H$, alkyl or aryl), O , S , SO , SO_2 , and NR (where $R = H$, alkyl or aryl);

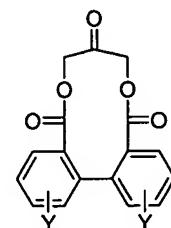
Sub P1 X
 R₁₁, R₁₂, R₁₃, or R₁₄ in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl), OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl), and halogen;

R₁₅, R₁₆, R₁₇, or R₁₈ in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl);



IV

R₁₉ or R₂₀ in formula (IV) is selected from alkyl, halogenated alkyl, aryl, CR₁R₂OCOR₃ (where R₁, R₂ or R₃ = H, alkyl or aryl), CR₁R₂OCOOR₃ (where R₁ or R₂ = H, alkyl or aryl; R₃ = alkyl or aryl), CR₁R₂NR₃COOR₄ (where R₁, R₂ or R₃ = H, alkyl or aryl, R₄ = alkyl or aryl), CR₁R₂NR₃COR₄ (where R₁, R₂, R₃ or R₄ = H, alkyl or aryl), and CR₁R₂NR₃SO₂R₄ (where R₁, R₂ or R₃ = H, alkyl or aryl, R₄ = alkyl or aryl); and



V

Y in formula (V) is selected from H, alkyl, halogenated alkyl, aryl, NO₂, CN, F, Cl, Br, I, COOR (where R = H or alkyl), OR (where R = H, alkyl or aryl), OSO₂R (where R = H, alkyl or

aryl), OSOR (where R = H, alkyl or aryl), OSR (where R = H, alkyl or aryl), SO₂R (where R = H, alkyl or aryl), SO₃R (where R = H, alkyl or aryl), SOON R₁R₂ (where R₁ or R₂ = H, alkyl or aryl), NR₁SOOR₂ (where R₁ = H, alkyl or aryl; R₂ = alkyl or aryl), NR₁SOR₂ (where R₁ = H, alkyl or aryl; R₂ = alkyl or aryl), CR₁R₂OR₃ (where R₁, R₂ or R₃ = H, alkyl or aryl), CR₁(OR₂)₂ (where R₁ = H or alkyl; R₂ = alkyl), CF₃, CF₂CF₃, OTf, OTs, OCOR (where R = H, alkyl or aryl), and OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl).

PL
Cmt
16. The method of claim 12 wherein said epoxidation reaction is carried out in a homogeneous solvent system containing dimethoxymethane-acetonitrile-water, acetonitrile-water, acetone-water, dioxane-water, dimethoxyethane-water, tetrahydrofuran-water, or a biphasic solvent system containing dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethylether-water, or mixtures thereof.

17. The method of claim 12 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

18. The method of claim 17 wherein said epoxidation reaction is carried out using potassium peroxomonosulfate as an oxidizing agent.

19. The method of claim 12 wherein said epoxidation reaction is carried out at a temperature within the range from about -10 °C to about 40 °C.

20. The method of claim 19 wherein said epoxidation reaction is carried out at room temperature.

21. The method of claim 12 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.

22. The method of claim 21 wherein said pH is within the range from about 7.0 to about 7.5.

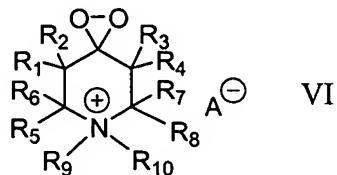
23. The method of claim 21 wherein said pH is controlled by using a pH-stat or a buffer.

24. The method of claim 23 wherein said buffer is selected from the solutions consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, and potassium carbonate, potassium hydroxide, and mixtures thereof.

25. The method of claim 12 wherein said epoxidation reaction provides said epoxides in at least about 5:1 β/α -epoxide ratio.

Sub A
26. A method of producing mostly $5\beta,6\beta$ -epoxides of steroids from Δ^5 -unsaturated steroids by an epoxidation reaction using a dioxirane under conditions effective to generate epoxides,

wherein said dioxirane is selected from compounds of generic formula VI,



R_1 or R_4 in formula (VI) is selected from alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH₂R (where R = aryl), OCONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl), OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl), and halogen;

R₂ or R₃ in formula (VI) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH₂R (where R = aryl), OCONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl), OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl), and halogen;

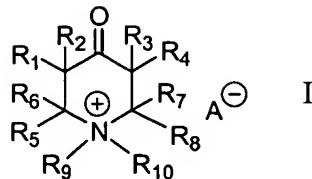
R_5, R_6, R_7 or R_8 in formula (VI) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl);

R_9 or R_{10} in formula (VI) is selected from alkyl, halogenated alkyl, and aryl; and

A in formula (VI) is selected from halogen, OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆.

27. The method of claim 26 wherein said dioxirane is generated in situ from a ketone and an oxidizing agent selected from potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

wherein said ketone is selected from compounds of generic formula I,



*PL
Cmt*

R_1 or R_4 in formula (I) is selected from alkyl, halogenated alkyl, aryl, OR (where $R = H$, alkyl or aryl), OCOR (where $R = H$, alkyl or aryl), OCOOR (where $R =$ alkyl or aryl), OCOOCH₂R (where $R =$ aryl), OCONR₁R₂ (where R_1 or $R_2 = H$, alkyl or aryl), OSiR₁R₂R₃ (where R_1 , R_2 or $R_3 =$ alkyl or aryl), and halogen;

R_2 or R_3 in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, OR (where $R = H$, alkyl or aryl), OCOR (where $R = H$, alkyl or aryl), OCOOR (where $R =$ alkyl or aryl), OCOOCH₂R (where $R =$ aryl), OCONR₁R₂ (where R_1 or $R_2 = H$, alkyl or aryl), OSiR₁R₂R₃ (where R_1 , R_2 or $R_3 =$ alkyl or aryl), and halogen;

R_5 , R_6 , R_7 or R_8 in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where $R = H$, alkyl or aryl), and CONR₁R₂ (where R_1 or $R_2 = H$, alkyl or aryl);

R_9 or R_{10} in formula (I) is selected from alkyl, halogenated alkyl, and aryl; and

A in formula (I) is selected from halogen, OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆.

28. The method of claim 26 wherein said epoxidation reaction is carried out in a solvent selected from acetonitrile, dimethoxymethane, acetone, dioxane, dimethoxyethane, tetrahydrofuran, dichloromethane, chloroform, benzene, toluene, diethylether, water, and mixtures thereof.

29. The method of claim 26 wherein said epoxidation reaction is carried out at a temperature within the range from about -40 °C to about 40 °C.

30. The method of claim 26 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.

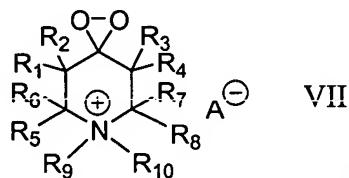
31. The method of claim 26 wherein said epoxidation reaction provides said epoxides in at least about 5:1 β / α -epoxide ratio.

32. A method of producing mostly $5\beta,6\beta$ -epoxides of steroids from Δ^5 -unsaturated steroids having a substituent at the 3α -position by an epoxidation reaction using a dioxirane under conditions effective to generate epoxides.

33. The method of claim 32 wherein said substituent is selected from OR (where R = H, alkyl or aryl), $O(CH_2)_nOR$ (where n = 1, 2 or 3, R = H, alkyl or aryl), $O(CH_2)_mSO_nR$ (where n = 1, 2 or 3; m = 0, 1 or 2; R = H, alkyl or aryl), $OSiR_1R_2R_3$ (where R_1 , R_2 or R_3 = alkyl or aryl), OSO_nR (where n = 0, 1 or 2; R = H, alkyl or aryl), OCO_nR (where n = 1 or 2; R = H, alkyl or aryl), $OCONR_1R_2$ (where R_1 or R_2 = H, alkyl or aryl), OPO_nR (where n = 2 or 3; R = alkyl or aryl), NR_1R_2 (where R_1 or R_2 = H, alkyl or aryl), $NR_1CO_nR_2$ (where n = 1 or 2; R_1 or R_2 = H, alkyl or aryl), $NR_1CONR_2R_3$ (where R_1 , R_2 or R_3 = H, alkyl or aryl), $NR_1SO_nR_2$ (where n = 1 or 2; R_1 = H, alkyl or aryl, R_2 = alkyl or aryl), $NPhth$ (Phth = phthaloyl group), $^+NR_1R_2R_3$ (where R_1 , R_2 , or R_3 = H, alkyl or aryl), $SiR_1R_2R_3$ (where R_1 , R_2 , or R_3 = H, alkyl or aryl), SO_nR (where n = 0, 1 or 2; R = H, alkyl or aryl), SCO_nR (where n = 1 or 2; R = H, alkyl or aryl), halogen, CN, NO_2 , alkyl, aryl, COOR (where R = H, alkyl or aryl), and $CONR_1R_2$ (where R_1 or R_2 = H, alkyl or aryl).

34. The method of claim 32 wherein said Δ^5 -unsaturated steroid having a substituent at the 3α -position is selected from the group consisting of Δ^5 -unsaturated steroids having a ketal derivative of ketone group or a thioketal derivative of ketone group at the 3-position.

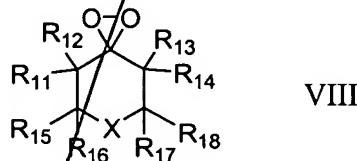
*Guib
P1*
35. The method of claim 32 wherein said dioxirane is selected from the group consisting of compounds of generic formula VII, VIII, IX and X.



R_1 , R_2 , R_3 , or R_4 in formula (VII) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH₂R (where R = aryl), OCONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl), OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl), and halogen;

R_5 , R_6 , R_7 , R_8 , R_9 or R_{10} , in formula (VII) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl);

A in formula (VII) is selected from halogen, OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆;



X in formula (VIII) is selected from (CR₁R₂)_n (where n = 1, 2, 3, 4, or 5; R₁ or R₂ = H, alkyl or aryl), O, S, SO, SO₂, and NR (where R = H, alkyl or aryl);

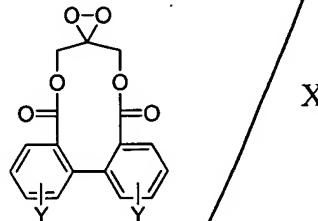
R_{11} , R_{12} , R_{13} , or R_{14} in formula (VIII) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl

or aryl), OCOOCH_2R (where $\text{R} = \text{aryl}$), OCONR_1R_2 (where R_1 or $\text{R}_2 = \text{H}$, alkyl or aryl), $\text{OSiR}_1\text{R}_2\text{R}_3$ (where R_1 , R_2 or $\text{R}_3 = \text{alkyl}$ or aryl), and halogen;

Detailed description of the chemical structure IX: A chemical structure showing a central carbon atom bonded to two R_{19} groups and two R_{20} groups. Each R_{19} group is bonded to one R_{20} group and one oxygen atom, which is further bonded to another oxygen atom, forming a peroxide group ($\text{O}-\text{O}$).

IX

R_{19} or R_{20} in formula (IX) is selected from alkyl, halogenated alkyl, aryl, $\text{CR}_1\text{R}_2\text{OCOR}_3$ (where R_1 , R_2 or $\text{R}_3 = \text{H}$, alkyl or aryl), $\text{CR}_1\text{R}_2\text{OCOOR}_3$ (where R_1 or $\text{R}_2 = \text{H}$, alkyl or aryl; $\text{R}_3 = \text{alkyl}$ or aryl), $\text{CR}_1\text{R}_2\text{NR}_3\text{COOR}_4$ (where R_1 , R_2 or $\text{R}_3 = \text{H}$, alkyl or aryl, $\text{R}_4 = \text{alkyl}$ or aryl), $\text{CR}_1\text{R}_2\text{NR}_3\text{COR}_4$ (where R_1 , R_2 , R_3 or $\text{R}_4 = \text{H}$, alkyl or aryl), $\text{CR}_1\text{R}_2\text{NR}_3\text{SO}_2\text{R}_4$ (where R_1 , R_2 or $\text{R}_3 = \text{H}$, alkyl or aryl; $\text{R}_4 = \text{alkyl}$ or aryl); and

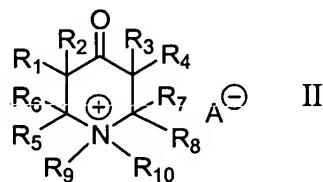


X

Y in formula (X) is selected from H , alkyl, halogenated alkyl, aryl, NO_2 , CN , F , Cl , Br , I , COOR (where $\text{R} = \text{H}$ or alkyl), OR (where $\text{R} = \text{H}$, alkyl or aryl), OSO_2R (where $\text{R} = \text{H}$, alkyl or aryl), OSOR (where $\text{R} = \text{H}$, alkyl or aryl), OSR (where $\text{R} = \text{H}$, alkyl or aryl), SO_2R (where $\text{R} = \text{H}$, alkyl or aryl), SO_3R (where $\text{R} = \text{H}$, alkyl or aryl), $\text{SOON R}_1\text{R}_2$ (where R_1 or $\text{R}_2 = \text{H}$, alkyl or aryl), NR_1SOOR_2 (where $\text{R}_1 = \text{H}$, alkyl or aryl; $\text{R}_2 = \text{alkyl}$ or aryl), NR_1SOR_2 (where $\text{R}_1 = \text{H}$, alkyl or aryl; $\text{R}_2 = \text{alkyl}$ or aryl), $\text{CR}_1\text{R}_2\text{OR}_3$ (where R_1 , R_2 or $\text{R}_3 = \text{H}$, alkyl or aryl), $\text{CR}_1(\text{OR}_2)_2$ (where $\text{R}_1 = \text{H}$ or alkyl; $\text{R}_2 = \text{alkyl}$), CF_3 , CF_2CF_3 , OTf , OTs , OCOR (where $\text{R} = \text{H}$, alkyl or aryl), and $\text{OSiR}_1\text{R}_2\text{R}_3$ (where R_1 , R_2 or $\text{R}_3 = \text{alkyl}$ or aryl).

36. The method of claim 32 wherein said dioxirane is generated in situ from a ketone and an oxidizing agent selected from potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

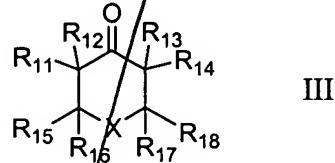
Sub A
37. The method of claim 36 wherein said ketone is selected from the group consisting of compounds of generic formula II, III, IV, and V,



R₁, R₂, R₃, or R₄ in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH₂R (where R = aryl), OCONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl), OSiR₁R₂R₃ (where R₁, R₂ or R₃ = alkyl or aryl), and halogen;

R₅, R₆, R₇, R₈, R₉ or R₁₀ in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl);

A in formula (II) is selected from halogen, OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆;

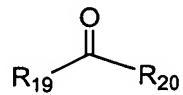


X in formula (III) is selected from (CR₁R₂)_n (where n = 1, 2, 3, 4, or 5; R₁ or R₂ = H, alkyl or aryl), O, S, SO, SO₂, and NR (where R = H, alkyl or aryl);

R₁₁, R₁₂, R₁₃, or R₁₄ in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or

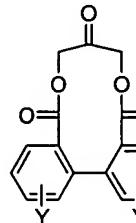
aryl), OCOCH_2R (where R = aryl), OCONR_1R_2 (where R_1 or R_2 = H, alkyl or aryl), $\text{OSiR}_1\text{R}_2\text{R}_3$ (where R_1 , R_2 or R_3 = alkyl or aryl), and halogen;

R_{15} , R_{16} , R_{17} , or R_{18} in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR_1R_2 (where R_1 or R_2 = H, alkyl or aryl);



IV

R_{19} or R_{20} in formula (IV) is selected from alkyl, halogenated alkyl, aryl, $\text{CR}_1\text{R}_2\text{OCOR}_3$ (where R_1 , R_2 or R_3 = H, alkyl or aryl), $\text{CR}_1\text{R}_2\text{OCOOR}_3$ (where R_1 or R_2 = H, alkyl or aryl; R_3 = alkyl or aryl), $\text{CR}_1\text{R}_2\text{NR}_3\text{COOR}_4$ (where R_1 , R_2 or R_3 = H, alkyl or aryl, R_4 = alkyl or aryl), $\text{CR}_1\text{R}_2\text{NR}_3\text{COR}_4$ (where R_1 , R_2 , R_3 or R_4 = H, alkyl or aryl), $\text{CR}_1\text{R}_2\text{NR}_3\text{SO}_2\text{R}_4$ (where R_1 , R_2 or R_3 = H, alkyl or aryl; R_4 = alkyl or aryl); and



V

Y in formula (V) is selected from H, alkyl, halogenated alkyl, aryl, NO_2 , CN , F, Cl, Br, I, COOR (where R = H or alkyl), OR (where R = H, alkyl or aryl), OSO_2R (where R = H, alkyl or aryl), OSOR (where R = H, alkyl or aryl), OSR (where R = H, alkyl or aryl), SO_2R (where R = H, alkyl or aryl), SO_3R (where R = H, alkyl or aryl), $\text{SOON R}_1\text{R}_2$ (where R_1 or R_2 = H, alkyl or aryl), NR_1SOOR_2 (where R_1 = H, alkyl or aryl; R_2 = alkyl or aryl), NR_1SOR_2 (where R_1 = H, alkyl or aryl; R_2 = alkyl or aryl), $\text{CR}_1\text{R}_2\text{OR}_3$ (where R_1 , R_2 or R_3 = H, alkyl or aryl), $\text{CR}_1(\text{OR}_2)_2$ (where R_1 = H or alkyl, R_2 = alkyl), CF_3 , CF_2CF_3 , OTf , OTs , OCOR (where R = H, alkyl or aryl), and $\text{OSiR}_1\text{R}_2\text{R}_3$ (where R_1 , R_2 or R_3 = alkyl or aryl).

38. The method of claim 32 wherein said epoxidation reaction is carried out in a solvent selected from acetonitrile, dimethoxymethane, acetone, dioxane, dimethoxyethane, tetrahydrofuran, dichloromethane, chloroform, benzene, toluene, diethylether, water and mixtures thereof.

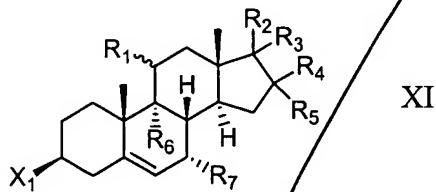
39. The method of claim 32 wherein said epoxidation reaction is carried out at a temperature within the range from about -40°C to about 40°C .

40. The method of claim 32 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.

41. The method of claim 32 wherein said epoxidation reaction provides said epoxides in at least about 5:1 β/α -epoxide ratio.

42. A method comprising:

producing mostly $5\beta,6\beta$ -epoxides of steroids by epoxidation reactions of Δ^5 -unsaturated steroids of generic formula XI catalyzed by ketones of generic formula XII, wherein



X_1 in formula (XI) is selected from H, OR (where R = H or alkyl), OCH_2OCH_3 , OCOR (where R = alkyl or aryl), $\text{OSiR}_1'\text{R}_2'\text{R}_3'$ (where R_1', R_2' or $\text{R}_3' =$ alkyl or aryl), halogen, CN, alkyl, aryl, and COOR (where R = H, alkyl or aryl);

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R_1 in formula (XI) is selected from H, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), OCH_2OCH_3 , halogen, CF_3 , and CF_2CF_3 ;

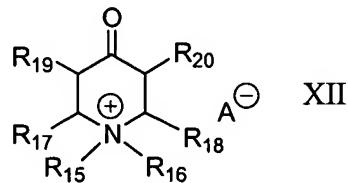
R_2 and R_3 in formula (XI) are each selected from the group consisting of H, alkyl, aryl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), $OSiR_1'R_2'R_3'$ (where R_1' , R_2' or R_3' = alkyl or aryl), COR (where R = alkyl), $COCH_2OR$ (where R = H or alkyl), $COCH_2OCOR$ (where R = alkyl or aryl), $COCH_2F$, COOR (where R = H or alkyl), $C(OCH_2CH_2O)R$ (where R = alkyl), $C(OCH_2CH_2O)CH_2OR$ (where R = H or alkyl), $C(OCH_2CH_2O)CH_2OCOR$ (where R = alkyl or aryl), and $C(OCH_2CH_2O)CH_2F$; or, are selected from the group consisting of O, OCH_2CH_2O , and $OCH_2CH_2CH_2O$;

R_4 in formula (XI) is selected from H, C_1-C_4 alkyl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), and $OSiR_1'R_2'R_3'$ (where R_1' , R_2' or R_3' = alkyl or aryl);

R_5 in formula (XI) is selected from H, C_1-C_4 alkyl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), and $OSiR_1'R_2'R_3'$ (where R_1' , R_2' or R_3' = alkyl or aryl);

R_6 in formula (XI) is selected from H, halogen, OR (where R = H or alkyl), and OCOR (where R = alkyl or aryl);

R_7 in formula (XI) is selected from H, halogen, OR (where R = H or alkyl), and OCOR (where R = alkyl or aryl);



R_{15} and R_{16} in formula (XII) are each selected from alkyl and aryl;

R_{17} and R_{18} in formula (XII) are each selected from H, alkyl, aryl, COOR (where R = H, alkyl or aryl), and $CONR_1R_2$ (where R_1 or R_2 = H, alkyl or aryl);

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R_{19} and R_{20} in formula (XII) are each selected from C_1-C_4 alkyl, halogenated alkyl, and halogen; and

A in formula (XII) is selected from OTf , BF_4 , OAc , NO_3 , BPh_4 , PF_6 , and SbF_6 .

43. The method of claim 42 wherein said C_1-C_4 alkyl is selected from the group consisting of methyl, ethyl, normal-propyl, iso-propyl, normal-butyl, iso-butyl, sec-butyl, and tert-butyl; and said aryl selected from the group consisting of phenyl, substituted phenyl, naphthyl, and substituted naphthyl groups.

44. The method of claim 42 wherein said epoxidation reactions are carried out in a homogeneous solvent system selected from the group consisting of dimethoxymethane-acetonitrile-water, acetonitrile-water, acetone-water, dioxane-water, dimethoxyethane-water, tetrahydrofuran-water, and mixtures thereof.

Sub A

45. The method of claim 42 wherein said epoxidation reactions are carried out in a biphasic solvent system selected from the group consisting of dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethylether-water, and mixtures thereof.

46. The method of claim 42 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

47. The method of claim 42 wherein said epoxidation reactions are carried out at a temperature within the range from about -10 °C to about 40 °C.

48. The method of claim 47 wherein said epoxidation reactions are carried out at room temperature.

49. The method of claim 42 wherein said epoxidation reactions are carried out at a pH within the range from about 7.0 to about 12.0.

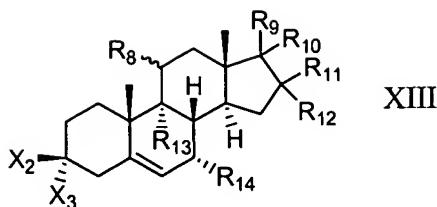
50. The method of claim 49 wherein said pH is within the range from 7.0 to 7.5.

51. The method of claim 49 wherein said pH is controlled by using a pH-stat or a buffer.

Sub A
52. The method of claim 51 wherein said buffer is selected from the group consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, potassium carbonate, potassium hydroxide, or mixtures thereof.

53. A method comprising:

producing mostly $5\beta,6\beta$ -epoxides of steroids by epoxidation reactions of Δ^5 -unsaturated steroids of generic formula XIII catalyzed by ketones of generic formula XIV, XV, XVI, and XVII, wherein



*X*₂ in formula (XIII) is selected from the group consisting of H, OR (where R = H or alkyl), OCH₂OCH₃, OCOR (where R = alkyl or aryl), OSiR₁'R₂'R₃' (where R₁', R₂' or R₃' = alkyl or aryl), halogen, CN, alkyl, aryl, and COOR (where R = H, alkyl or aryl), and,

*X*₃ in formula (XIII) is selected from the group consisting of OR (where R = H or alkyl), OCH₂OCH₃, OCOR (where R = alkyl or aryl), OSiR₁'R₂'R₃' (where R₁', R₂' or R₃' = alkyl or aryl), halogen, CN, NO₂, alkyl, and aryl; or,

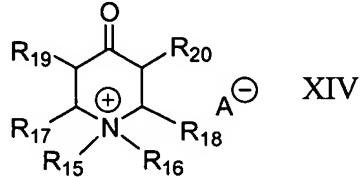
*X*₂ and *X*₃ in formula (XIII) are selected from the group consisting of O, OCH₂CH₂O, and OCH₂CH₂CH₂O;

*R*₈ in formula (XIII) is selected from H, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), OCH₂OCH₃, halogen, CF₃, and CF₂CF₃;

*R*₉ and *R*₁₀ in formula (XIII) are each selected from the group consisting of H, alkyl, aryl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), OSiR₁'R₂'R₃' (where R₁', R₂' or R₃' = alkyl or aryl), COR (where R = alkyl), COCH₂OR (where R = H or alkyl), COCH₂OCOR (where R = alkyl or aryl), COCH₂F, COOR (where R = H or alkyl), C(OCH₂CH₂O)R (where R = alkyl), C(OCH₂CH₂O)CH₂OR (where R = H or alkyl), C(OCH₂CH₂O)CH₂OCOR (where R = alkyl or aryl), and C(OCH₂CH₂O)CH₂F; or *R*₉ and *R*₁₀ in formula (XIII) are selected from the group consisting of O, OCH₂CH₂O, and OCH₂CH₂CH₂O;

*R*₁₁ and *R*₁₂ in formula (XIII) are each selected from the group consisting of H, C₁–C₄ alkyl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), and OSiR₁'R₂'R₃' (where R₁', R₂' or R₃' = alkyl or aryl);

*R*₁₃ and *R*₁₄ in formula (XIII) are each selected from the group consisting of H, halogen, OR (where R = H or alkyl), and OCOR (where R = alkyl or aryl);

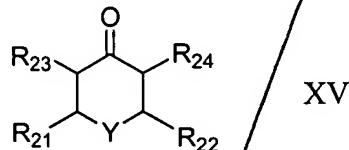


*R*₁₅ or *R*₁₆ in formula (XIV) is selected from alkyl and aryl;

*R*₁₇ or *R*₁₈ in formula (XIV) is selected from H, alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl);

*R*₁₉ or *R*₂₀ in formula (XIV) is selected from H, C₁–C₄ alkyl, halogenated alkyl, and halogen; and

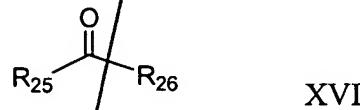
A in formula (XIV) is selected from OTf, BF₄, OAc, NO₃, BPh₄, PF₆, and SbF₆;



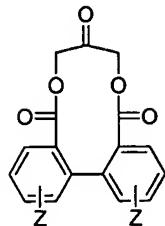
Y in formula (XV) is selected from CH₂, O, S, SO, SO₂, and NR (where R = H or alkyl);

*R*₂₁ or *R*₂₂ in formula (XV) is selected from H, alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR₁R₂ (where R₁ or R₂ = H, alkyl or aryl);

*R*₂₃ or *R*₂₄ in formula (XV) is selected from H, halogen, C₁–C₄ alkyl, halogenated alkyl, and OCOR (where R = alkyl or aryl);



*R*₂₅ or *R*₂₆ in formula (XVI) is selected from C₁–C₄ alkyl, halogenated alkyl, CH₂OCOR (where R = alkyl or aryl); and



XVII

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 Z in formula (XVII) is selected from H, C₁–C₄ alkyl, aryl, NO₂, CN, F, Cl, Br, I, COOR (where R = alkyl), CH₂OR (where R = H or alkyl), CH(OR)₂ (where R = alkyl), CF₃, CF₂CF₃, OTf, OTs, OCOR (where R = alkyl or aryl), and OSiR₁R₂R₃' (where R₁', R₂' or R₃' = alkyl or aryl).

54. The method of claim 53 wherein said C₁–C₄ alkyl is selected from the group consisting of methyl, ethyl, normal-propyl, iso-propyl, normal-butyl, iso-butyl, sec-butyl, and tert-butyl; and said aryl selected from the group consisting of phenyl, substituted phenyl, naphthyl, and substituted naphthyl groups.

55. The method of claim 53 wherein said epoxidation reactions are carried out in a homogeneous solvent system selected from the group consisting of dimethoxymethane-acetonitrile-water, acetonitrile-water, acetone-water, dioxane-water, dimethoxyethane-water, and tetrahydrofuran-water, and mixtures thereof.

56. The method of claim 53 wherein said epoxidation reactions are carried out in a biphasic solvent system selected from the group consisting of dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethylether-water, and mixtures thereof.

57. The method of claim 53 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

58. The method of claim 53 wherein said epoxidation reactions are carried out at a temperature within the range from about -10 °C to about 40 °C.

59. The method of claim 58 wherein said epoxidation reactions are carried out at room temperature.

60. The method of claim 53 wherein said epoxidation reactions are carried out at a pH within the range from about 7.0 to about 12.0.

61. The method of claim 60 wherein said pH is within the range from 7.0 to 7.5.

62. The method of claim 60 wherein said pH is controlled by using a pH-stat or a buffer.

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63. The method of claim 62 wherein said buffer is selected from the group consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, potassium carbonate, potassium hydroxide, or mixtures thereof.